
(12) UK Patent Application (19) GB (11) 2 002 809 A

(21) Application No 7830721

(22) Date of filing
21 Jul 1978

(23) Claims filed
21 Jul 1978

(30) Priority data
2733105

(32) 22 Jul 1977

(33) Fed Rep of Germany
(DE)

(43) Application published
28 Feb 1979

(51) INT CL² C10K 1/34

(52) Domestic classification
C5E PG

(56) Documents cited

GB 1155584

GB 951665

GB 851443

GB 744333

GB 476684

GB 384532

(58) Field of Search
C5E

(71) Applicants
BASF Aktiengesellschaft
6700 Ludwigshafen
Federal Republic of
Germany

(72) Inventors
Guentar Zirker
Hans Gettert
William Samecki
Hans J Henrici
Hans Heiner Reich

(74) Agents
J Y & G W Johnson

(54) **Manufacture of synthesis gas
by partial oxidation**

(57) In the manufacture of synthesis gas containing CO and H₂ by partially oxidizing hydrocarbons or coal with oxygen-containing gas in the presence of a temperature moderator in a non-packed, non-catalytic, synthesis gas reactor at an autothermal temperature of from 900 to 1700°C and at a pressure of from 1 to 250 bars, then cooling the reaction product, separating off particulate carbon, removing acidic impurities and carrying out any further desired aftertreatment, difficulties have arisen over removal of hydrocyanic acid. The present invention removes hydrocyanic acid from the reaction product by treating it, after the step of separating off particulate carbon but before the step of removing acidic impurities, in a cata-

lytic hydrogenation zone at from 100 to 250°C and a pressure of from 1 to 250 bars.

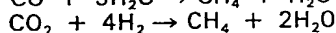
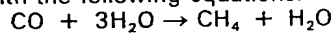
GB 2 002 809 A

SPECIFICATION

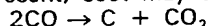
Manufacture of synthesis gas by partial oxidation

- 5 The present invention relates to a continuous process for the manufacture of synthesis gas containing carbon monoxide, hydrogen and possibly methane, and provides a process wherein the hydrocyanic acid and ammonia impurities present in the crude synthesis gas are removed by a catalytic hydrogenation before washing the gas.
- 10 The manufacture of synthesis gas is described in Ullmanns Encyklopädie der technischen Chemie, Volume 16, 3rd edition, 1965, pages 599-635. More recent developments relating to various fields of use are dealt with in the Supplementary Volume, 3rd edition 1970, under the headings "Ammonia" or "Methanol", in the section on "Gas Production", on pages 468 et seq., and pages 94/95, respectively.
- 15 Attention is drawn in particular to Figure 1 given on page 601 of the first-mentioned literature reference, which Figure gives a survey of gas production when using various starting materials, eg. coal or liquid or gaseous hydrocarbons.
- 20 At the present time, synthesis gas or heating gas is produced industrially by partially oxidizing hydrocarbons, e.g. natural gases or LPG, or coal with oxygen-containing gas. Steam, nitrogen or some other suitable material may be added to the reaction mixture to act as a temperature moderator.
- 25 However, even in the case of increasing proportions of heavier hydrocarbons of the type of heavy fuel oil or even residual oils or vacuum residues have been used to produce gas. This trend will continue in the future. These heavy oils contain a relatively larger proportion of residual organic nitrogen compounds and have a higher sulfur content than the lighter hydrocarbons.
- 30 For this reason, the oxidation reaction produces not only carbon monoxide, hydrogen and methane but also, depending on the raw material and its composition, carbon dioxide, hydrogen sulfide and traces of carbon oxysulfide, ammonia, hydrocyanic acid and formic acid. Part of the carbon present in the raw material arises as soot and must be removed before further working up of the gas.
- 35 Regardless of the nature of the further processing, the gas is purified at some stage of the process to remove the acidic compounds, eg. CO_2 , H_2S , HCN and HCOOH (at times with the exception of carbon dioxide) and also carbon oxysulfide. If the said compounds are to be removed conjointly by washing the gas, substantial difficulties arise, especially if the hydrocyanic acid content is relatively high. These are attributable to the fact that the hydrocyanic acid is readily soluble in most solvents used to purify the gas and is therefore only removed incompletely from the solvent when the latter is regenerated. Consequently, the hydrocyanic acid accumulates in the wash solution; in aqueous wash solutions, it is hydrolyzed to formic acid, which also accumulates.
- 40 The accumulation of hydrocyanic acid and formic acid in the wash solution reduces the ability of the latter to take up acidic compounds; it also causes severe corrosion of the equipment used for gas purification. The amount of formic acid which passes from the gas production stage to the gas purification stage is insignificant compared to the hydrocyanic acid.
- 45 The invention therefore proposes to remove the hydrocyanic acid from the gas before the remaining acidic compounds, eg. H_2S or CO_2 , are removed. Removing the hydrocyanic acid by washing with cold water before washing the acidic gas entails additional expense; the wash liquid must be regenerated because it can, as a rule, not be discharged as effluent, and furthermore operating the washing process with fresh water only is uneconomical.
- 50 German Laid-Open Application DOS 2,352,425 discloses converting nitrogen compounds, eg. NH_3 and HCN , even in gases containing H_2S , to nitrogen over a transition metal sulfide as the catalyst (iron sulfide being proposed in particular). This reaction is in the main carried out at from 649 to 815°C. In addition, USSR Patent 439,302 describes the removal of HCN from gases not specified in detail, using Cr-Ni catalysts at from 250 to 450°C. According to the patentees' statements, the activity of the catalyst used decreases very greatly even after an operating time of only 20 hours. Finally, German Laid-Open Application DOS 2,245,859
- 55 discloses reacting hydrocyanic acid over supported catalysts, containing elements of sub-group 6 and/or 8 in the form of the oxides, and removing it from certain gas mixtures. This process is carried out at atmospheric pressure. The examples use model gases which do not contain any carbon oxides or any steam. The above Laid-Open Application discloses that only above 200°C or above 250°C does the reaction take place with the desired conversions. Space velocities of at most 1,500 per hour may be used.
- 60 All these processes have disadvantages which mitigate against their industrial use. The present invention therefore proposes removing the hydrocyanic acid, before the gas enters the acidic impurities removal step, e.g. the acidic gas wash, by bringing the gas into contact with a catalyst over which the hydrocyanic acid is hydrogenated by means of hydrogen which is in any case present in the gas.
- 65

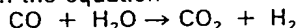
A catalyst for this purpose must be resistant to sulfur and must be selected for the desired reaction, namely the hydrogenation of hydrocyanic acid, since a number of other reactions over catalysts, which would undesirably alter the composition of the gas containing carbon oxides and steam, are thermodynamically possible. First, the carbon oxides can react with hydrogen to form methane, in accordance with the following equations:



In addition, if there is little water present, soot may deposit in accordance with the equation



If on the other hand the gas has a high steam content, the conversion of the carbon monoxide may take place in accordance with the equation



All the above reactions are undesirable in view of the object of the invention.

We have found that hydrocyanic acid can be selectively hydrogenated even at low temperatures and high throughputs, and even in the presence of carbon oxides and steam. This was unexpected in view of the disclosures in German Laid-Open Applications DOS 2,352,425 and DOS 2,245,859.

The present invention therefore provides a process for the manufacture of synthesis gas containing carbon monoxide, hydrogen and possibly methane by partially oxidizing hydrocarbons or coal with oxygen-containing gas in the presence of steam or of another temperature moderator in a non-packed, non-catalytic, synthesis gas reactor at an autothermal temperature of from 900 to 1,700°C and at a pressure of from 1 to 250 bars, cooling the reaction product, separating off particulate carbon, removing acidic impurities and carrying out any further desired aftertreatments, wherein the reaction product is treated in a catalytic hydrogenation zone at from 100 to 250°C and a pressure of from 1 to 250 bars for hydrogenation of hydrocyanic acid, after the step of separating off the particulate carbon but before the step of removing the acidic impurities from the gas.

In this catalytic hydrogenation zone, the hydrocyanic acid present in traces is hydrogenated by hydrogen present in the gas; this does not substantially alter the concentration of the remaining constituents of the gas.

The catalytic hydrogenation zone may be packed with a hydrogenation catalyst of a type which is conventionally used for desulfurization and denitrification processes in refinery technology. Such refining catalysts generally contain at least one transition metal from group 6 and/or 8 of the periodic table, as a rule in the form of their oxides and/or sulfides, on a carrier, suitably consisting of an inorganic refractory oxide.

The transition metals of group 6 are chromium, molybdenum and tungsten, amongst which molybdenum preferred. Examples of transition metals of group 8 are nickel and cobalt.

Preferably the catalysts contain at least one transition metal both of group 6 and group 8, as a rule in the ratio of from 0.8 to 10 atoms of the metal(s) of group 6 per atom of the metal(s) of group 8. The atomic ratio should advantageously be from 1:1 to 4:1. The use of catalysts which contain nickel and molybdenum, or cobalt and molybdenum, in the above atomic ratios, is particularly preferred.

The oxides and/or sulfides of the metals which act as hydrogenation catalysts as a rule account for from 10 to 45% by weight of the total catalysts; the carrier accounts for the remainder, namely from 90 to 55% by weight.

Suitable carriers for the above are, in particular, ceramic compositions, for example MgO, SiO₂, Al₂O₃, TiO₂, ZrO₂ and their mixtures, eg. a mixture of MgO and Al₂O₃, or compounds, namely the spinels, as well as artificial or synthetic magnesium silicates and aluminum silicates, eg. clays and bleaching earths, as well as aluminas, eg. γ-Al₂O₃ and δ-Al₂O₃, hydrated aluminas, eg. bayerite, hydrargillite or boehmite, or mixtures of aluminas or of hydrated aluminas. The most preferred carriers are aluminas, hydrated aluminas and mixtures of these.

The catalytic hydrogenation zone is operated at from 100 to 250°C, preferably from 150 to 230°C. These temperatures relate to the temperature at which the autothermal cracking products enter, after removal of particulate carbon (soot). Since it is desirable that neither methanization nor conversion should take place in the catalytic hydrogenation zone, these entry temperatures are also virtually identical with the exit temperatures. The pressure in the catalytic hydrogenation zone is generally from 1 to 250 bars and is preferably set so that it corresponds to the pressure prevailing in the generator, minus the normal pressure loss during processing. The space velocity is generally from 1,000 to 20,000 per hour (volumes of gas at 1 bar and 0°C). Higher pressure favours catalytic hydrogenation of hydrocyanic acid so that the higher the gasification pressure used, the lower the temperature, and the higher the space velocity, which can be selected. At low gasification pressures, however, the temperature should preferably not be higher than 200°C.

Raw materials suitable for the autothermal cracking include hydrocarbon gases, LPG, gasoline hydrocarbons, fuel oils, heavy fuel oils, vacuum gas oils, vacuum residues and coal.

- Depending on the raw material used, and on the process conditions especially the gasification pressure, the composition of the crude gas after passing the gasification zone, ie. downstream from the water quench or from the waste heat system, may vary within the following ranges: H_2 = from 62 to 40 per cent by volume, CO = from 34 to 60 per cent by volume, CH_4 = from 0.2 to 10 per cent by volume and CO_2 = from 2 to 6 per cent by volume. The remaining constituents, eg. N_2 , H_2S , noble gases and the like as a rule each account for less than 1% by volume. The hydrocyanic acid content of the crude gas depends on the nitrogen content of the starting material and may be from 1 to 50 ppm by volume or, in the case of heavy fuel oil, in particular from 10 to 50 ppm by volume.
- 10 The Examples which follow illustrate the process of the invention. Catalysts A ($CoMo/Al_2O_3$) and B ($Ni/MoAl_2O_3$) were prepared as described below, and had the properties also shown below, %s being by weight:
- Catalyst A
- 15 Boehmite was precipitated from an aluminum salt solution by means of ammonia, and was filtered off and washed salt-free. The alumina paste, whilst still moist, was mixed with cobalt nitrate and with a molybdenum salt solution. The powder was kneaded and extruded, and the extrudate was dried and calcined.
- The catalyst obtained contained 5% of cobalt oxide and 13.5% of MoO_3 , the remainder being the Al_2O_3 carrier, contaminated with 2% by weight of SiO_2 . The catalyst had a bulk density of 20 650 kg/m^3 , a specific surface area of $220\text{ m}^2/\text{g}$ and a pore volume of $0.5\text{ cm}^3/\text{g}$.
- Catalyst B
- Alumina extrudates were produced from alumina paste, and calcined, as described under A above. The calcined extrudates were impregnated with a solution containing nickel and molybdenum and were then dried and again calcined. This gave a catalyst which contained 25 of NiO and 15% of MoO_3 , the remainder being alumina contaminated with SiO_2 . The catalyst had a bulk density of 700 kg/m^3 , a specific surface area of $150\text{ m}^2/\text{g}$ and a pore volume of $0.6\text{ cm}^3/\text{g}$.
- In all Examples, the gas leaving the reaction zone contained less than 1 ppm (by volume) of HCN and its composition corresponded, within the limits of analytical accuracy, to that of the 30 feed gas. In all experiments, the catalyst was employed in the sulfidized form. However it must be borne in mind that even a catalyst employed as the oxide is gradually converted to its sulfide form on prolonged operation, as a result of the sulfur compounds contained in the crude synthesis gas. To accelerate the reaction, the catalyst can however be employed, from the start, in its sulfidized form.
- 35
- ### EXAMPLE 1
- Heavy fuel oil (residues obtained under atmospheric pressure) was preheated to 110°C and passed, through a ring burner, into a non-packed, non-catalytic synthesis gas reactor. The density of the oil starting material was 954 kg/m^3 at 16°C (17 degrees API), the kinematic 40 viscosity at 80°C was $64.0\text{ m}^2/\text{s}$ (8.45 degrees Engler) and the gross calorific value was $43,618\text{ kJ/kg}$. An analysis gave the following composition in % by weight: 85.50 C, 11.46 H, 1.75 S, 0.35 N, 0.90 O and 0.09 ash. Steam at 400°C , and virtually pure oxygen (99.1 mole % pure) were fed to the generator at the same time. The weight ratio H_2O/fuel was 0.40 and the atomic ratio of oxygen to carbon (in the fuel) was 0.9072.
- 45 The reaction between the feed streams took place in the reaction zone under an absolute pressure of about 45 bars and at an autogenous temperature of $1,306^\circ\text{C}$. The mean residence time in the reaction zone was about 6 seconds. Partial oxidation converted the hydrocarbon feed stream into a gas stream which after indirect cooling to 165°C and subsequent removal of the particulate carbon by means of water had the following composition, in mole % of dry gas: 3.6 50 CO_2 , 47.5 CO , 48.0 H_2 , 0.2 CH_4 , 0.4 H_2S and COS , 0.16 N_2 and 0.14 Ar. The gas contained the following trace impurities, in ppm by volume, 3 NH_3 , 18.5 HCN and less than 0.5 $HCOOH$. It is to be noted that some of the said trace impurities are removed from the gas when the particulate carbon separates out. Under the stated operating conditions, the particulate carbon only accounted for 1.5% of the carbon employed, and since more than 90% was recycled to 55 the gasification, it did not substantially affect the material balance. After removing the particulate impurities, the gas obtained, having the above composition, was water-saturated and was at 82°C and under an absolute pressure of about 42.5 bars.
- 4 kmole/h of this gas stream were heated to 150°C by indirect heat exchange and fed to a hydrogenation zone containing 9 liters of catalyst A. The operating pressure corresponded to the 60 generator pressure minus the normal pressure loss of the intermediate equipment; its absolute value was about 42.5 bars. The above throughput corresponded to a space velocity of 10,000 liters per liter of catalyst per hour.

EXAMPLE 2

- 65 4 kmole/hour of a stream of gas prepared under the same conditions; and having the same 65

composition, as the gas stream of Example 1 were heated to 150°C by indirect heat exchange, and fed to a hydrogenation zone containing 9 liters of catalyst B. The absolute pressure was 42.5 bars, and the said throughput corresponded to a space velocity of 10,000 liters per liter of catalyst per hour.

- 5 The composition of the gas before and after the hydrogenation zone can be seen from the table below. 5

		prior to hydrogenation	after hydrogenation	
10	CO ₂	3.6	3.6	10
	CO	47.5	47.5	
	H ₂	48.0	48.0	
	CH ₄	0.2	0.2	
15	H ₂ S + COS	0.4	0.4	15
	N ₂	0.16	0.16	
	Ar	0.14	0.14	
	HCN	18.5	≥1	

- 20 On leaving the hydrogenation zone the gas was freed from all acidic components including CO₂ in an amine wash. No enrichment of hydrocyanic acid or formic acid was observed in the wash liquor. Nor was there any sign of corrosion. 20

25 CLAIMS 25

1. A process for the manufacture of synthesis gas or heating gas containing carbon monoxide, hydrogen and possibly methane by partially oxidizing hydrocarbons or coal with oxygen-containing gas in the presence of steam or of another temperature moderator in a non-packed, non-catalytic, synthesis gas reactor at an autothermal temperature of from 900 to 1,700°C and at a pressure of from 1 to 250 bars, then cooling the reaction product, separating off particulate carbon, removing acidic impurities and carrying out any further desired aftertreatments, wherein the reaction product is treated in a catalytic hydrogenation zone at from 100 to 250°C and a pressure of from 1 to 250 bars for hydrogenation of hydrocyanic acid after the step of separating off the particulate carbon but before the step of removing the acidic impurities from the gas. 30 35

2. A process as claimed in claim 1, wherein the treatment in the catalytic hydrogenation zone is carried out at from 150 to 230°C.

3. A process as claimed in claim 1 or 2, wherein the catalytic hydrogenation zone is packed with a catalyst which contains from 10 to 45% by weight of one or more transition metals of group 6 and/or 8 of the periodic table, in the form of their oxides and/or sulfides, and from 90 A 40 to 55% by weight of a carrier.

4. A process as claimed in claim 3, wherein the catalyst contains at least one transition metal of group 6 and at least one transition metal of group 8 in an atomic ratio of from 0.8:1 to 10:1.

5. A process as claimed in claim 3 or 4, wherein the catalyst contains molybdenum and either nickel or cobalt. 45

6. A process as claimed in any of claims 1 to 5, wherein the catalytic hydrogenation zone is operated at from 1 to 250 bars pressure and a space velocity of from 1,000 to 20,000 per hour (volumes of gas at 1 bar and 0°C).

7. A process for the manufacture of synthesis gas or heating gas carried out substantially as described in either of the foregoing Examples. 50

8. Synthesis gas or heating gas when manufactured by a process as claimed in any of claims 1 to 7.